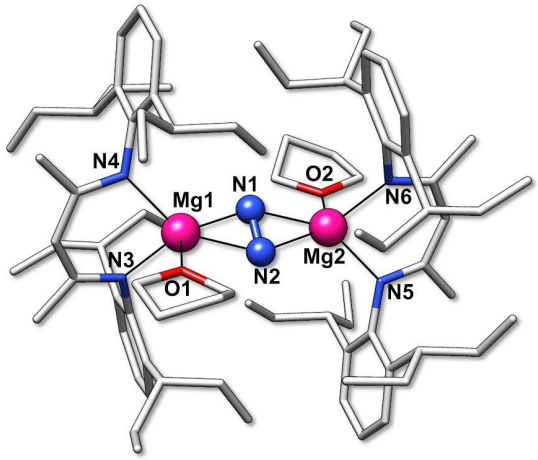
SI - Activation of the N_2 molecule by means of low-valence complexes of calcium and magnesium

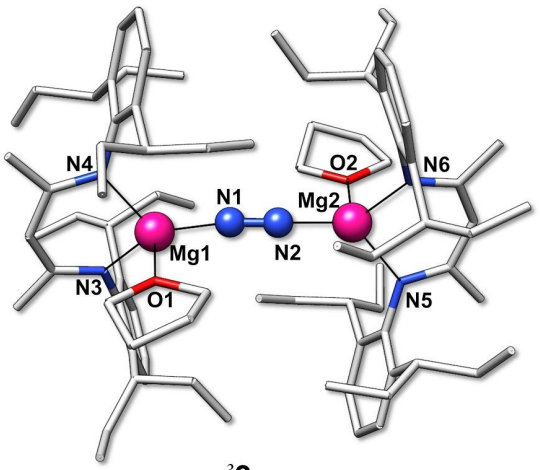
Table S1 - Geometry parameters obtained by optimizing species $\mathbf{2}_{Ca}$ and $\mathbf{3}_{Ca}$ at the BP86-D3(BJ)/def2-TZVP/def2-SVP level of theory.

	$\mathbf{2}_{Ca}$		$\mathbf{3}_{Ca}$	
	Exp		*Exp*	
N1=N2	1.27	1.26	1.26	1.26
Ca1–N1	2.30	2.30	2.30	2.28
Ca1–N2	2.31	2.31	2.30	2.29
Ca2–N1	2.31	2.31	2.30	2.29
Ca2–N2	2.30	2.30	2.30	2.29
Ca1–N3	2.40	2.39	2.39	2.38
Ca1–N4	2.42	2.42	2.40	2.37
Ca2–N5	2.40	2.40	2.40	2.37
Ca2–N6	2.42	2.42	2.40	2.37
Ca1–O	2.40	2.39	2.39	2.39
Ca2–O	2.41	2.39	2.39	2.39

Figure S1 - Graphical representation of the observed N_2 coordination mode at the [(BDI)Mg(THF)] compound. Colour pattern: grey, C; blue, N; red, O; magenta, Mg. Hydrogen atoms are omitted for clarity.



$\mathbf{3}_{Mg\text{-}N2}$

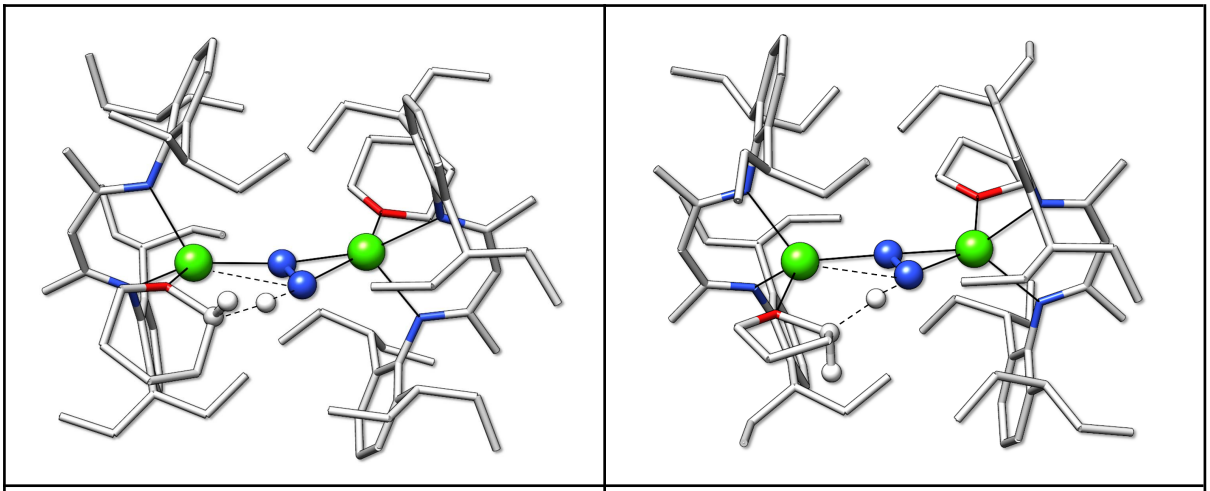


$e^3\mathbf{3}_{Mg\text{-}N2}$

Table S2 - Natural atomic charges and natural atomic orbital occupancies (in brackets) computed for $e^3\mathbf{2}_{Mg\text{-}N2}$ and $e^3\mathbf{3}_{Mg\text{-}N2}$.

	$e^3\mathbf{2}_{Mg\text{-}N2}$	$e^3\mathbf{3}_{Mg\text{-}N2}$
Mg1	1.80 (10)	1.80 (10)
Mg2	1.80 (10)	1.80 (10)
N1	-0.87 (8)	-0.85 (8)
N2	-0.87 (8)	-0.87 (8)

Figure S2 - Graphical representation of the transition state **2TS** and **3TS**. Colour pattern: grey, C; blue, N; red, O; green, Ca. Hydrogen atoms are omitted for clarity.



2TS | **3TS**

Figure S3 - Graphical representation of protonation reaction product $e^1 2I_{Mg}$ and $e^1 3I_{Mg}$. Colour pattern as in Figure S1.

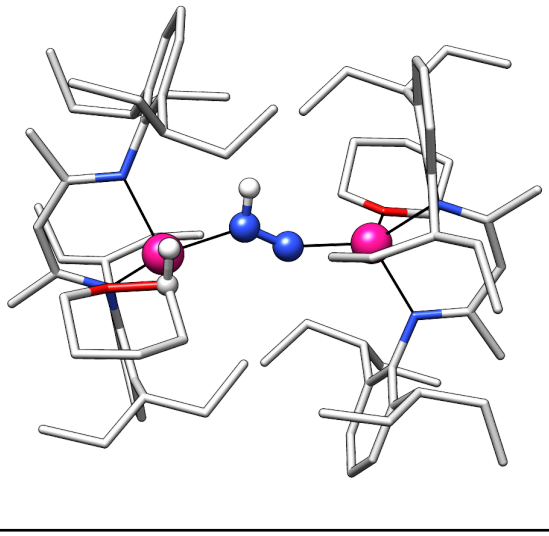
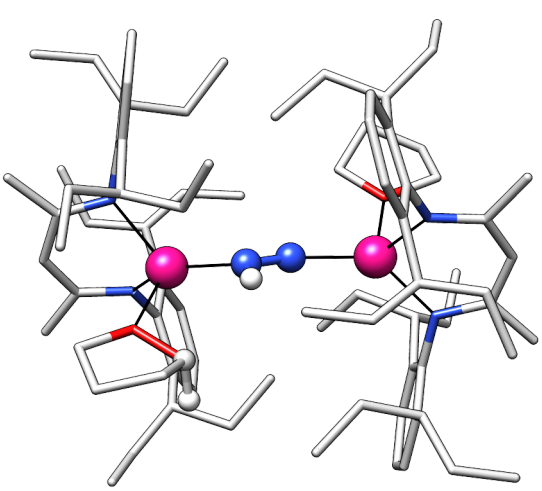
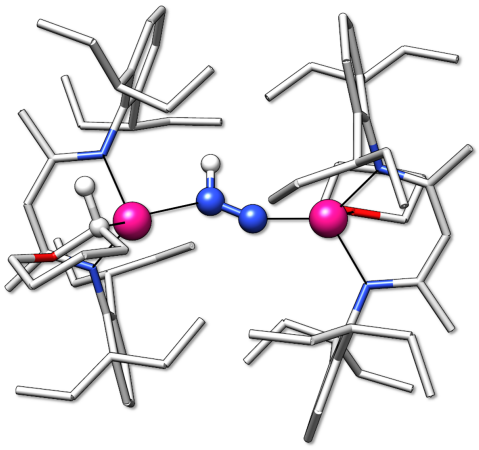
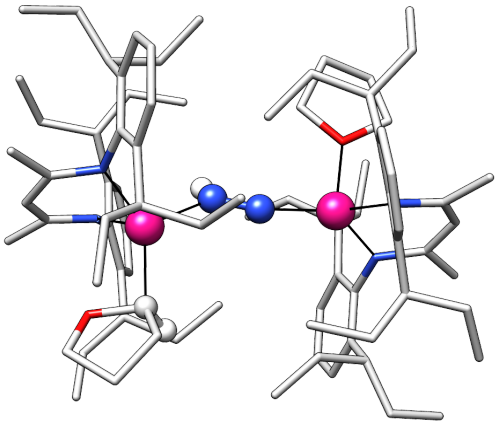
	
$e^1 2I_{Mg}$	$e^1 3I_{Mg}$

Figure S4 - Graphical representation of protonation reaction product $e^3 2P_{Mg}$ and $e^3 3P_{Mg}$. Colour pattern as in Figure S1.

	
$e^3 2P_{Mg}$	$e^3 3P_{Mg}$